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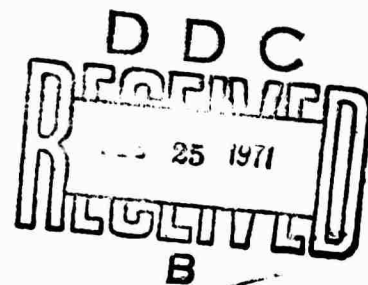
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## I. Introduction

This report describes work done under the sponsorship of ARPA Order No. 418 during the last half of 1970. Substantial progress has been made in all areas of glass science under investigation. X-ray and neutron diffraction studies have demonstrated a degree of ordering in glassy  $\text{SiO}_2$ , while experimental and theoretical studies of radiation-induced defects in this important material have been advanced considerably. The first observation has been made of free carrier optical absorption in semiconducting chalcogenide glasses and the existence of a new fundamental defect center in alkali borate glasses has been confirmed. A potential new laser glass has been formulated and optimized with respect to immunity from platinum contamination; efforts to prepare and test large batches have been initiated. These and other results are described in greater detail in the following sections.

There have been no personnel changes of major consequence to the program during this reporting period.

## II. Progress

### A. Structure of Silica Glass

X-ray and neutron diffraction data have been collected with a high degree of statistical accuracy for silica glass. The analytical procedure, based on assuring the consistency of the radial distribution function with known physical and mathematical properties of the system under study, has resulted in reproducible features in the radial distribution curves for both x-ray and neutron scattering which indicate a degree of ordering in the silica glass. The ordered phase has been tentatively identified and studies are presently proceeding to establish the character of the ordering and its approximate amount. These include investigations with related crystal systems and spectroscopic investigations.

Additional experiments have been carried out demonstrating the relative insensitivity of the structure of silica glass to previous history. Two different sources of sample were used, glass made both from fused quartz and from evaporated  $\text{SiO}_2$ . The samples were heated to about  $2000^\circ\text{C}$  for several minutes and to about  $1450^\circ\text{C}$  for several days. In the latter case cristoballite formed on the surface and made the sample opaque. However, when the cristoballite was scraped off and the transparent inner portion was revealed, the same radial distribution

curve was obtained as that for the original glass samples and the samples heated to about  $2000^{\circ}\text{C}$  for a short period of time. The heat treatments which were employed, followed by simple cooling in air, did not apparently alter the bulk structure of the silica glass samples.

#### B. Semiconducting Glasses

The far infrared transmission studies of the chalcogenide glasses  $\text{As}_2\text{Se}_3$  and  $\text{Tl}_2\text{SeAs}_2\text{Te}_3$  have revealed the existence of localized vibrational absorption peaks in both glasses, and a thermally activated, frequency independent, free carrier absorption in the highly conducting  $\text{Tl}_2\text{SeAs}_2\text{Te}_3$  glass. In contrast to the Lorentzian lineshapes observed in the vibrational spectra of crystalline materials, the lineshapes observed in the glasses are best fitted by a Gaussian distribution of Lorentzian oscillators. The Gaussian line width provides a new fundamental parameter to characterize the disorder in these materials. The thermally activated absorption represents the first free carrier or electronic optical effect to be observed in a semiconducting glass, and its frequency independence confirms the low values of mobility measured in semiconducting glasses by transport techniques.

During the current contract period the infrared studies of these phenomena have been extended over a broad range of

temperature. The localized absorption peaks associated with the As-Se nearest neighbor vibrational mode in glassy  $\text{As}_2\text{Se}_3$  ( $237\text{ cm}^{-1}$ ) and  $\text{Tl}_2\text{SeAs}_2\text{Te}_3$  ( $246\text{ cm}^{-1}$ ) have been investigated at temperatures ranging from  $4.2^\circ\text{K}$  to  $400^\circ\text{C}$ . In  $\text{As}_2\text{Se}_3$  the width and intensity of the absorption peak remains essentially unchanged at the highest temperature attained, which was some  $200^\circ\text{K}$  above the glass transition temperature. However, in the  $\text{Tl}_2\text{SeAs}_2\text{Te}_3$  glass, there is a relatively well-defined temperature near  $250^\circ\text{C}$ , (about  $150^\circ\text{K}$  above the glass transition temperature) above which the vibrational absorption peaks disappear rapidly with increasing temperature. Apparently the structural unit or local order which gives rise to the vibrational absorption peaks is maintained in the melt up to some critical temperature, above which the local order disintegrates and the peak vanishes.

Previously the thermally activated absorption in the  $\text{Tl}_2\text{SeAs}_2\text{Te}_3$  glass had been studied only in the 3 to 15 micron range of relative transparency. The disappearance at high temperature of the vibrational absorption peaks made it possible to extend (at high temperature) the study of this free carrier effect to the longer wavelength region which is obscured by the restrahten bands at lower temperature. The range of wavelengths over which this thermally activated absorption is frequency independent has

been found to extend at least to 100 microns. In addition, the activation energy, which in the 3 to 15 micron range was equal to that for dc conductivity ( $\approx 0.35$  eV), is also constant out to 100 microns. The magnitude of the conductivity throughout this spectral range is a factor of forty larger than the dc value at the same temperature. This large thermally activated conductivity in the infrared does not appear to be consistent with a one-electron description of the conduction process in the glass.

#### C. Radiation Damage in Alkali Borate Glasses

The study of radiation-induced defects in alkali borate glasses has been a continuing part of the ARPA-supported glass research at NRL. During the recent contract period, investigations of the newly-discovered boron electron center (BEC) were completed and a lengthy manuscript dealing with its properties has reached a late stage in preparation; analysis of a number of halide-related hole traps has been pushed forward, and still another intrinsic defect center (this one involving alkalis) has been discovered.

The BEC, previously termed the "boron E' center", has been renamed to reflect recent findings that the upper limit on the total unpaired spin density on the boron is smaller than previously estimated. While not ruling out the "E' center model"

of an electron localized in a "dangling" boron  $sp^3$  orbital, the refined data now give some added support to a somewhat similar model wherein the electron is trapped in a boron-oxygen anti-bonding orbital.

A careful search for the BEC in "pure"  $B_2O_3$  glass ended with negative results, suggesting that the presence of four-coordinated borons and/or alkali ions must be necessary to produce the defect. Indeed, either of the two models under consideration probably requires charge compensation by alkali ions to assure electrical neutrality and hence stability. Further indication of alkali involvement in the BEC is the increase in boron hyperfine coupling constant when potassium is replaced by sodium or sodium is replaced by lithium in glasses having the same molar fraction of alkali oxide. Since the observed linewidths lead to an estimated upper limit of about eight percent for the spin density on any alkali, it is concluded that the alkali ion(s) which is evidently associated with this center must reside a slight distance away and exerts its principal influence electrostatically.

Neither of the models proposed for the BEC necessarily incorporates the ideas of oxygen vacancies or broken bonds; given a suitable disposition of alkali ions, electrons can conceivably be

trapped in pre-existing dangling orbitals (on three coordinated borons) or in any of the boron-oxygen antibonding orbitals. Therefore, in view of the observed dramatic changes in boron hyperfine coupling constant with glass composition, it can be reasonably suggested that the BEC is behaving as a "probe" of the structure of the (undamaged) glass. The structural details being probed are probably the several types of boron-oxygen ring structures previously postulated to exist in the alkali borate system.

Studies of radiation-induced defects in halide-doped alkali borate glasses are also reaching the publication stage. The production of a number of halide-related paramagnetic hole centers has been described in some detail in the previous two Semiannual Reports. In a new development, the relative numbers of boron-oxygen hole centers (BOHCs), BECs,  $X^{\circ}$ , and  $X_2^{-}$  ( $X$  = halogen) were determined for glasses doped with KF, KCl, KBr, and KI, as well as undoped glasses, x-irradiated near  $25^{\circ}\text{K}$ . The relative hole-trapping efficiencies of halide ions under these conditions were found to be  $\text{I} > \text{Br} > \text{Cl} > \text{F} \approx 0$ , consistent with the suggestion that free holes generated by irradiation at low temperatures are initially trapped at the available sites with the largest geometric cross sections. In as much as the trapping



efficiency of the BOHC was found to be roughly the equivalent to that for  $\text{Br}^-$ , these experiments have succeeded in establishing its approximate cross section. The production efficiency of the BEC, on the other hand, was virtually unaffected by whether or not any type of halide ion was present. This provides independent verification that the BEC is an electron-type center, since, if it were of the hole-type, its production would have been suppressed by addition of such a high-cross section hole trap as  $\text{I}^-$ . These findings together with activation-energy information derived from isochronal annealing data should lead to a far better understanding of the radiation-damage processes in borate glasses.

The final area in which progress has been made concerns the discovery of yet another intrinsic defect center. The newest center, like the BEC (which can by itself account for no more than 25% of the trapped electrons), is also of the electron type. It may be termed the alkali electron center (or AEC) and can be noted in glasses containing  $\geq 20\%$  alkali oxide. Hyperfine interactions with potassium and sodium are readily apparent for the AEC in the appropriate glass systems; the AEC may also exist in the lithium borate system but, if so, its spectrum is difficult to distinguish from that of the BEC. It has been tentatively suggested that the AEC is a di-alkali molecular ion or an alkali

atom. Studies of this very interesting new fundamental defect center are continuing.

#### D. Defect Centers in Simple Silicate Glasses

Silicate glasses exhibit at least three classes of radiation induced defect centers: (1) those characteristic of flaws in the basic Si-O network, (2) those resulting from the presence of substitutional impurities, and (3) those arising from the addition of network modifiers which can rupture Si-O bonds, creating non-bridging oxygens in the process. The simplicity of the spectra in irradiated high purity  $\text{SiO}_2$  suggests that categories (2) and (3) represent the majority of centers found in silicate glasses. Therefore this work was undertaken to investigate the nature of the radiation induced defects in  $\text{SiO}_2$  containing small traces of Li, Na, and K (network modifiers) as well as  $\text{SiO}_2$  containing aluminum which is the principal substitutional impurity in most silicate glasses. Optical absorption and EPR measurements were used to identify the respective defects.

The presence of alkali in the Si-O network has been related to the formation of several common radiation induced defect centers in alkali silicate glasses. In doped fused silica samples, the intensity of the  $E_2'$  band at 5.4 eV and the paramagnetic hole

center at  $g = 2.01$  have been shown to be directly proportional to alkali content. The  $E_2'$  band has been shown to exist in high purity alkali silicate glass and may result from a complex center which consists of an electron trapped in a silicon tetrahedral orbital at a non-bridging oxygen vacancy with alkali and protons nearby. It may represent a major electron trap in silicate glasses. The dependence of the hole resonance on alkali concentration and the observed variation of broadening with alkali type support the hypothesis that the holes are trapped on non-bridging oxygens in the vicinity of an alkali ion.

The 7.6 eV band in the vacuum ultraviolet was measured for the first time in alkali doped silica. The intensity of this band was relatively constant in samples of varying alkali content which indicates the defect is probably characteristic of the Si-O network.

This work is described in a paper recently submitted for publication.

#### E. Thin Glass Films

Both  $\text{SiO}_2$  and alkali silicate glass films were deposited on LiF substrates in thicknesses ranging from  $100\text{\AA}$  to a few microns. The optical properties of these films were studied both before and after x-irradiation. These sputtered films seem to differ from bulk glasses in the vacuum ultraviolet region of

the spectrum. They do not exhibit any resolvable absorption bands such as observed in  $\text{SiO}_2$  and silicate glasses in the 6 - 20 eV region. This may arise because of the complete lack of any ordering in the films or because of the existence of strains in the films. Strained Si-O bonds are often suggested as the precursors to radiation induced damage in  $\text{SiO}_2$ . These films tend to show much more coloration for a given radiation dose than their bulk counterparts, suggesting that strains might be present.

A series of vanadium phosphate glass films were deposited on  $\text{SiO}_2$  substrates. Both optical and EPR measurements were made on these films. Samples were annealed in both oxidizing and reducing atmospheres to study the valence changes taking place in the vanadium ions and in an effort to identify absorption bands observed in the 5 to 6 eV region of the spectrum. This work is still in progress.

#### F. Ultraviolet Spectra of Silicate Glasses

Much of the NRL work during the past few years on the ultraviolet spectra of high purity  $\text{SiO}_2$ , alkali doped  $\text{SiO}_2$  and alkali silicate glasses is summarized in a paper recently submitted to the Journal of Physics and Chemistry of Solids. This work has been discussed in previous reports and will not be treated here.

### G. Theory of Bond-Breaking Processes in $\text{SiO}_2$

A continuing theoretical investigation concerning the elementary processes taking place in pure  $\text{SiO}_2$  and the silica based glasses has centered on an initial attempt to describe the bond breaking process in terms of the familiar molecular orbital description usually associated with the well-known one electron band picture. The latter has been quite successful in describing optical absorption in, for example, the alkali halides. In this picture, the electrons are associated with molecular orbitals in the form of Bloch wave functions, and the optical transitions of the system are interpreted in terms of one electron transitions between energy bands. The positions of these energy levels do not change significantly as a result of the transitions. The bond breaking processes have been used in describing both the ultraviolet spectrum in  $\text{SiO}_2$  and the optical excitation of the  $E'_1$  center in this material.

It has proven to be quite difficult to describe the bond breaking process in terms of the molecular orbital picture. This is primarily because of the fact that a molecular orbital involves each atom in the material, while the bond breaking process is a very localized one, involving one or at the most two atoms. In fact, it appears that bond breaking is not a fundamental process in

this picture and its description within this framework would be quite complicated. Thus far, there has not been any direct experimental evidence for the bond breaking process. However, the examination of the excited state of the  $E'_1$  center in  $\text{SiO}_2$  could provide this evidence. According to the recently published model, the bond breaking process would manifest itself in the optical excitation by means of a change in the hyperfine splitting of the electron spin resonance spectrum. Because the experimental verification of the bond breaking process is important in determining whether, in fact, the historically successful molecular orbital picture is a good one for describing certain processes in a material such as  $\text{SiO}_2$ , the experiment, itself, has attracted the attention of at least one group outside of NRL.

#### H. Other Theory

The theoretical study of the Van Vleck paramagnetic susceptibility in solid materials has centered upon examining in some detail the nature of the kinetic energy change of the system brought about by solidification. An earlier conjecture concerning the alkali halides assigned virtually all the kinetic energy of crystallization to the rotational or nonspherical component. The recent study has involved a more detailed analysis of the nondiagonal matrix elements of the kinetic and potential energy

operators. These have been demonstrated to be zero. This result is of importance in an analysis of the rotational kinetic energy component which is intimately connected with the Van Vleck susceptibility.

A theoretical examination of the transition probabilities for soft x-ray emission in  $\text{SiO}_2$  has involved the application of the valence bond model. The ratio of the transition probabilities for the two oxygen  $K_\alpha$  emission lines was calculated to be 3:1, in fairly good agreement with observation. Analysis of the Si  $K_\beta$  and  $L_{II, III}$  emission lines is underway.

The work on atomic wavefunctions has continued with an analysis of the ten electron atom (Ne and isoelectronic ions). The application of the already successful method of calculation of two particle correlations in the two electron atom together with a sum rule analysis makes possible an analysis for larger atoms. The calculation of two particle correlations as well as the leading term in the energy expansion for this isoelectronic series of atoms is underway. These results, coupled with the application of the already proved charge density theorem will make possible the calculation of highly accurate nonrelativistic wave functions for these atoms.

#### I. Preparation, Purification, and Analysis of Glass

In the latter half of the present reporting period the complete overhaul and refurnishing of the laboratory devoted to the synthesis of glass and its raw materials was undertaken.

Accordingly such activities as raw material synthesis, and glass synthesis involving wet chemical procedures has been seriously restricted. Included in the above category is the development of high purity  $B_2O_3$ . Glass preparation involving dry mixing and the use of available raw materials either purchased or prepared earlier is still conducted since furnace operations were not interrupted. Progress reported in this area refers to preparations either made under the above circumstances or in the period prior to the laboratory dislocation.

The demonstration that a newly developed laser glass composition can be melted in platinum crucibles without suffering from contamination by metallic platinum remains incomplete due to the fact that analytical techniques of known high sensitivity have not yet been successfully applied to the determination of platinum in the glass. It had been demonstrated that the technique of melting in a CO-CO<sub>2</sub> reducing atmosphere produced glass in which neutron activation and mass spectrographic analysis techniques sensitive to 10 - 20 parts of platinum per billion parts of glass could not positively detect contamination in bulk portions of a glass sample. However, depending upon the glass composition, as much as ten micrograms of platinum metal could be detected



on the surface of some melts. The analytical technique employed is sensitive to one microgram of platinum, and microscopic examination of the glass surfaces was able to detect the presence of platinum on sample surfaces which proved to bear less than the one microgram sensitivity limit. Accordingly the development of the contamination resisting composition was based on microscopic examination, but the development of more sensitive techniques is continuing.

Our technique of known high sensitivity is neutron activation analysis. The above reported result with this method was obtained at NRL, but since the NRL reactor is no longer in operation, the activation services at the National Bureau of Standards have been sought. A set of glass samples which include compositions similar to commercial laser glasses as well as the series of compositions which led to the development of the resistant glass have been submitted to the Bureau. The only result to date was the report of an expected high platinum content in the NRL prepared sample having the composition of the commercial lithium, calcium aluminosilicate laser glass. Delays in the operation of the reactor and refinement of the analytical procedure have held up the results of the other samples.

The earlier analytical technique employed at NRL for the determination of surface platinum contamination involved dissolving the platinum deposit and measuring its concentration by a colorimetric method employing stannous chloride. This method was sensitive to one microgram of platinum. A newly developed technique is to dissolve the deposit, concentrate the platinum solution, and determine the platinum content with an emission spectrograph. This procedure has increased the analytical sensitivity to one tenth of a microgram, and is now being applied to the glass samples. Results are not yet conclusive, but the method is believed to be reliable. It is hoped that the best samples will have even lower platinum contamination than can be detected by this method. If this proves to be correct and if results from the Bureau are not forthcoming a method involving dissolving, concentrating, and the use of the mass spectrograph will be considered.

The formulation of a glass resistant to platinum contamination was based on the employment of the least volatile and most stable alkali and alkaline earth ions, and the use of these ions in the minimum concentration consistent with the preparation of a good quality glass at the lowest possible melting temperature. The successful composition was one mole of combined alkali and

alkaline earth ions to five of silicon plus aluminum. While it proved necessary to make some variations of the silica to alumina ratio in order to obtain a suitably meltable glass, the first attempted concentrations of the alkali and alkaline earths proved successful. In any glass development program, it is usual to investigate the compositional parameters in detail in order to determine the composition having optimum properties and to provide patent specifications. A very limited amount of such compositional work has now been done, but optimum properties such as freedom from platinum or laser performance cannot be completely evaluated at this time. It was found that when the alkali to alkaline earth contents were maintained in a ratio of 4 - 1, that the original 1 - 3 ratio of  $\text{Li}_2\text{O}-\text{Na}_2\text{O}$  could not be substantially varied in the direction of higher lithium without encountering devitrification. Variation of this ratio in the direction of higher sodium was not attempted, because this direction would favor platinum contamination. Considerable latitude on variation of the original 1 - 2 ratio of  $\text{MgO}$  to  $\text{CaO}$  was possible without affecting glass quality. The above information is sufficient to describe the successful preparation of the glass as not excessively sensitive to small compositional variation. However, it is unlikely that

sufficient effort can be provided in order to determine the entire latitude of permissible compositional variation in this nine component glass as would be required in a patent application.

In the development of the above glass, one of the most important considerations is a low melting temperature. Glass contamination is ascribed to a reaction between the platinum crucible and oxygen derived from dissociation of volatile alkali and alkaline earth ions, and the volatility, the dissociation, and the reaction will all be favored by higher melting temperatures. Accordingly the most reactive raw materials available were used in the development program. The raw material of most variable reactivity is silica. Silica used in the glass industry is usually sand or quartz, but a special fine amorphous synthetic silica was used in our laboratory. It was therefore of interest to determine whether the more common sources of silica could be employed without increasing the melting temperature. It was found that the glass could be synthesized using either ground quartz or sand instead of the synthetic silica. It was not necessary to increase the melting temperature, but the melting time required for the same size sample was about fifty percent longer. No platinum contamination of the surfaces of the samples made with these alternate silica sources could be detected with the available microscopic test.

Of the common laser glass formulations, it had been determined that surface platinum contamination in reducing atmosphere melting was greatest with a lithium calcium aluminosilicate composition. This is consistent with its high alkali content and melting temperature of  $1400^{\circ}\text{C}$ . However, the commercial availability and employment of this glass renders it of sufficient importance to consider preparation variations which might eliminate its platinum contamination. Accordingly, some attempts have been made to reduce the melting temperature of this glass by using reactive silica and pre-reacting the mixed batch by a variety of mixing and sintering techniques before melting. It was found that, with the above procedures, the melting temperature could be reduced to  $1100^{\circ}\text{C}$ , but that even at this temperature platinum contamination was easily detected microscopically. The effect of the lower melting temperature reduced contamination, but did not eliminate it.

The mass spectrographic analysis of commercial lithium calcium aluminosilicate glasses is now complete. One of the two samples received contained the usual combination of activators used in this glass, cerium and neodymium, while the other was doped with only cerium. About 4 ppm of Pt was found in the sample doped with cerium alone and about 2 ppm in the glass containing both

cerium and neodymium. Other impurities detected were copper, lead, barium, and lanthanum. The latter two ions are known to be not harmful in laser glasses. The copper present was in the order of 3 - 5 parts per million and the lead content did not exceed 0.5 ppm. The effect of such impurity concentrations is not known, and moreover no information on the valence state of these two ions is revealed by the mass spectrograph. The glass is reported to be melted in a nitrogen atmosphere. Under this melting atmosphere the copper is probably present as both cuprous and cupric ion, but a portion of the lead could be atomic. A sufficient concentration of atomic lead could lead to aggregates producing inclusion type damage similar to the effect of platinum metal. However, lead has not been previously reported in the analysis of glass areas showing inclusion type damage, and the concentration detected above is probably insignificant. The main impurity problem with this glass remains platinum. The above glass samples analyzed were polished rods, and while they were thoroughly cleaned in sampling, the possibility of contamination introduced in processing after melting is not completely eliminated. It seems likely that the glass is sufficiently pure that any damage mechanisms which might be associated with impurities such as copper and lead are overshadowed by the effect of platinum.

Traces of copper impurity have been shown to be present in all the high purity glasses prepared in this program. They are demonstrated by the appearance of a weak luminescence under ultraviolet radiation. Glasses prepared in other laboratories also show copper activated luminescence unless they contain high concentrations of interfering ions which mask the effect. The role which this copper impurity may have under conditions of heavy ultraviolet exposure such as the operation of a glass laser has never been considered. Accordingly, an investigation of such behavior of copper in the lithium, calcium, aluminosilicate laser glass matrix has been undertaken. The luminescence changes produced by radiation are more easily observed with high copper doping levels and with x-ray treatment rather than ultraviolet. However it has been shown that ultraviolet produces results similar to those obtained by x-rays, and the centers observed with high copper contents could exist in low undetectable concentrations in the samples of much lower copper content.

Glass samples containing up to 4 mole percent of copper were prepared in a reducing atmosphere. All of these, including an undoped sample, showed a blue luminescence due to  $\text{Cu}^+$  ion with 254 nm excitation. With longer wavelength excitation, 320 nm,

a yellow emission is observed in samples containing 550 ppm or more of copper. The center responsible for the yellow emission is not known. Exposure to 254 nm ultraviolet, or to x-rays produces a new luminescent center excitable at 365 nm and emitting in the red. Electron spin resonance measurements indicate that the ultraviolet or x-ray irradiation increases the cupric ion concentration of the glass. The conversion of cuprous to cupric ion in glass by ultraviolet has been previously reported from absorption measurements, but the present ESR results provide the additional information that the cuprous and cupric ions occupy similar sites in the glass. The nature of the red emitting center produced by radiation is not known. Since cupric ion is known not to be an activator of luminescence in glass prepared to contain the cupric ion, the possibility that the radiation created cupric ions are luminescent centers is not favored. More likely centers are probably  $\text{Cu}^0$  or  $\text{Cu}^{3+}$ , but detection methods for the presence of such species are not immediately available. The demonstrated photochemical changes in copper suggest that copper impurities can provide charge trapping in the operation of laser glass. Whether the present copper impurity concentrations in such glasses can provide harmful effects is not yet known.



The attempt to produce transparent glass ceramics containing phototropic crystallizer barium titanate has been discontinued. It proved possible by appropriate heat treatment of glass compositions in the barium oxide-boron oxide-titanium oxide system to produce crystals of a variety of habits. In some cases the preparations had reasonably good transparent regions, but no phototropic samples were obtained. Concurrently, preparations of high purity barium and strontium titanate have been doped with all the ions and combinations of ions reported to produce phototropic material, but no light sensitive products were obtained. The above results indicate that the phototropic behavior of the titanates is not sufficiently well understood to warrant continued development of the glass ceramic, and a detailed investigation of the phototropy of titanates does not appear to be a suitable activity within the glass program.

J. Contract with Bausch and Lomb

Bausch and Lomb is currently engaged in the preparation of platinum free glass in larger sample sizes than made previously. The glass composition (3.4%  $\text{Li}_2\text{O}$ , 10.3%  $\text{Na}_2\text{O}$ , 1.2%  $\text{MgO}$ , 2.3%  $\text{CaF}_2$ , 3.2%  $\text{Al}_2\text{O}_3$ , 79.6%  $\text{SiO}_2$ ) and the technique of melting in a  $\text{CO-CO}_2$  atmosphere were both developed at NRL. The

present results are encouraging. Stirred melts as large as 400 g have been made and appear to be free of bubbles and striae. The expectation is that this glass will be capable of routine preparation in as good optical quality as any other glass made in the same size of melting facility.

Smaller melts are being made in the same furnace to check variations of composition and melting procedure. No surface platinum contamination has been observed, but two metallic specks which proved to contain nickel, iron, and chromium were found. NRL used procedures of batch presintering, gas purification, and furnace flushing do not appear to be essential to the glass synthesis.

Plans for the immediate future call for analysis of glass surfaces for platinum and inspection of the bulk glass for platinum particles with an ultramicroscope. If these techniques reveal that the glass appears to be platinum free, the next test procedure would involve exposure to high energy laser pulses.

### III. Publications and Oral Presentations

Far Infrared and Microwave Optical Properties of Vitreous  $\text{As}_2\text{Se}_3$ , P. C. Taylor, S. G. Bishop, and D. L. Mitchell, Solid State Comm. 8, 1783 (1970).

Far Infrared and Microwave Conductivity Spectrum of Semiconducting  $\text{Tl}_2\text{SeAs}_2\text{Te}_3$  Glass, S. G. Bishop, P. C. Taylor, and D. L. Mitchell, J. Non-Cryst. Solids, (in press).

Far Infrared and Microwave Optical Properties of Vitreous  $\text{As}_2\text{Se}_3$ , P.C. Taylor, S.G. Bishop, and D.L. Mitchell, Gordon Research Conf., Issaquah, Washington, 27-30 July 1970.

Vibrational and Free Carrier Optical Properties of Vitreous  $\text{Te}_2\text{SeAs}_2\text{Te}_3$ , P.C. Taylor, S.G. Bishop, D.L. Mitchell, and L.H. Slack, Tenth Int. Conf. on Physics of Semiconductors, M.I.T., Cambridge, Mass., 17-21 August 1970.

Contamination of Glass by Platinum, R.J. Ginther. Presented at meeting of Glass Division of the American Ceramic Society, Bedford Springs, Pa., October 1970. Abstract in American Ceramic Society Bulletin, September 1970, p. 820.

Color and Optical Absorption Caused by Cations in High-density, Lead Silicate Glass, J.S. Stroud (Bausch and Lomb, Inc.). Presented at meeting of Glass Division of the American Ceramic Society, Bedford Springs, Pa., October 1970. Abstract in American Ceramic Society Bulletin, September 1970, p. 815.

Radiation Induced Defect Centers in Alkali Doped Fused Silica, George Sigel. Presented at the American Ceramic Society Fall Meeting of the Glass Division, Bedford, Pa., October 1970.

Vacuum Ultraviolet Absorption in Alkali Doped Fused Silica and Silicate Glasses, George Sigel. Submitted to J. Phys. Chem. Solids.

The Role of Alkali in the Formation of Radiation Induced Defect Centers in Simple Silicate Glasses, George Sigel. Submitted for publication in the 9th International Glass Congress Proceedings.

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ESR Studies of an Intrinsic Trapped-Electron Center in X-Irradiated Alkali Borate Glasses, D.L. Griscom. To be submitted to J. Chem. Phys.

Model for the  $\text{E}_2'$  Centers in  $\text{SiO}_2$ , A.R. Ruffa. Phys. Rev. Lett. 25, 650 (1970).